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Introduction

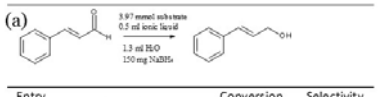
The selective hydrogenation of *α,β*-unsaturated aldehydes and ketones is of high importance in the fine chemical industry especially in the production of pharmaceuticals, fragrances and flavors. [1] Traditionally, expensive noble metal based catalysts are used such as palladium and platinum. However it can be difficult to prevent the formation of the fully saturated alcohol formed by further reduction of the unsaturated alcohol. In current industrial practice, the reduction of *α,β*-unsaturated aldehydes and ketones is performed either under high hydrogen pressures or by hydrogen transfer reaction using alcohol as a hydride donor, with both methods resulting in reduced selectivity towards hydrogenation of the carbonyl group. Hence in this work we have shown an efficient and green method for highly selective reduction of *α,β*-unsaturated aldehydes and ketones at room temperature in a range of ionic liquids and in the absence of noble metal catalysts, using $NaBH_4$ as a reducing agent. Most notably, using $[P_{6,6,6,14}][N(CN)_2]$ ionic liquid, within 10 min, 97% conversion of cinnamaldehyde was achieved with 100% selectivity towards cinnamyl alcohol. The ionic liquid was easily recycled without any noticeable decline in activity. The reduction protocol was further extended to a variety of *α,β*-unsaturated aldehydes and ketones.

Materials and Methods

The ionic liquids used in this study were prepared and characterized in QUB. For example $[P_{6,6,6,14}][N(CN)_2]$ was prepared by reaction of $[P_{6,6,6,14}]Cl$ (5 g, 9 mmol) in excess $Na[N(CN)_2]$ (1.2 g, 13 mmol) in chloroform/water. The water layer was separated from the organic layer which contained the ionic liquid. The organic layer was subsequently washed several times with water to remove any residual alkali halide. The chloroform was removed by rotary evaporation and the ionic liquid was dried overnight at 75 °C. The ionic liquids were characterized using a range of techniques; nuclear magnetic resonance (NMR), CHN elemental analysis, theromogravimetric analysis (TGA), differential scanning calorimetry (DSC). All ionic liquids were found to be pure and exhibit thermal stability up to and beyond 300 °C with $[P_{6,6,6,14}]_2[CoN(CN)_2)_4]$ and $[P_{6,6,6,14}][NTf_2]$ also having glass transitions at -71 °C and -69 °C respectively. Reduction of *α,β*-unsaturated aldehydes and ketones was performed in a 25 cm^3 glass reactor. In a typical experiment, the reactor was charged with substrate (3.97 mmol), 15 cm^3 dibutyl ether and ionic liquid (0.5 cm^3) and stirred using a magnetic stirrer at 20 °C. Fresh $NaBH_4$ (1:1 mole equivalent) was dissolved in deionized water (1.3 cm^3) and added to the glass reactor. The reaction was monitored by taking regular samples and analyzing by GC.

Results and Discussion

Table 1 summarizes the results of the hydrogenation of cinnamaldehyde in a range of ionic liquids giving the product selectivity to cinnamyl alcohol and the conversions after 40 min. In most cases the reactions in the presence of ionic liquid were found to have a dramatically enhanced rate of reaction compared to in the absence of ionic liquid. For example, in the absence of ionic liquid (entry 1) the conversion was just 5% after 40 min. While in the presence of $[P_{6,6,6,14}][N(CN)_2]$, after 40 min the conversion was 83% and 97% selective towards cinnamyl alcohol (entry 2). The reaction with $[P_{6,6,6,14}][N(CN)_2]$ was further enhanced by allowing the ionic liquid and cinnamaldehyde to stir for 1 h before the addition of reducing agent. The conversion increased to 97% and was 99% selective to cinnamyl alcohol after just 10 min.



Entry	Ionic liquid	Conversion (%)	Selectivity (%)
1	blank	5	99
2	$[P_{6,6,6,14}][N(CN)_2]$	83	97
3	$[P_{6,6,6,14}][N(CN)_2]$*	97	99
4	$[P_{6,6,6,14}]_2[Co(N(CN)_2)_4]$	97	84
5	$[P_{6,6,6,14}]_2[Co(N(CN)_2)_4]$·2$[P_{6,6,6,14}][N(CN)_2]$	95	82
6	$[P_{6,6,6,14}]NTf_2$	25	100
7	$[C_3CNmin][FeCl_4]$	11	85

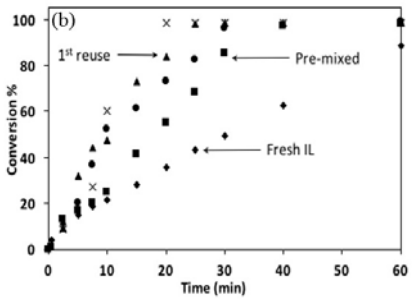


Figure 1 (a) Reduction of cinnamaldehyde using different ionic liquids (b) cinnamaldehyde % conversion-time profile for the reusability of $[P_{6,6,6,14}][N(CN)_2]$ ionic liquid.

Extension of this method to other substrates was successful for example, in the case of ketoisophorone after 60 min 100% conversion was achieved with 97% selectivity towards hydroxyisophorone. The reduction of citral was found to be 82% selective towards geraniol and nerol with 86% conversion achieved after 60 min. The $[P_{6,6,6,14}][N(CN)_2]$ ionic liquid was found to show excellent reusability. As shown in Figure 1(b), first recycle of the ionic liquid showed a significant enhancement in reaction rate compared to the fresh cycle. The increased rate has been attributed to an increased liquid-liquid mass transfer of cinnamaldehyde from the organic phase and BH_4^- nucleophiles from aqueous phase into the ionic liquid phase. It is likely that the ionically charged supramolecular network of ionic liquids greatly accelerates the nucleophilic substitution (S_N^2) reaction not only by enhancing the hydride transfer from aqueous phase, but also increasing the stability of hydride anion. In a separate control experiment, wherein the organic phase containing cinnamaldehyde was pre-mixed with ionic liquid and stirred for 1 h to equilibrate before addition of $NaBH_4$. This showed significant increase in reaction rate. In all recycle experiments, selectivity towards cinnamyl alcohol remained consistently in the range of 96-99% and conversions in the range of 89-99%.

Significance

A highly selective hydrogenation protocol for reduction of a range of *α,β*-unsaturated aldehydes and ketones at room-temperature has been developed. In the absence of organic solvent, using $[P_{6,6,6,14}][N(CN)_2]$, 100% selectivity to cinnamyl alcohol at 97% cinnamaldehyde conversion was achieved within 10 minutes. To the best of our knowledge, such high selectivities at room temperature, without using noble metal catalysts, are unprecedented in literature and hold very high significance for chemical industry. Using $[P_{6,6,6,14}][N(CN)_2]$ the method was successfully extended to other of *α,β*-unsaturated aldehydes and ketones and was easily recyclable with increased reaction rates and no notable loss of selectivity.

References

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